

## CLAIMS

1. A method for obtaining reproducibility of the retention times of the components of a mixture to be analysed in an apparatus for gaschromatographic analysis provided with a capillary column,  
 5 when one or more of the following variations occurs: a variation in the length of the column, or alternatively replacement of the column with a column having identical real specifications with the exception of the length, and/or a variation in the output pressure from said column, given that the pneumatic resistance  $K_{old} = K(L_{old})$  of said column is  
 10 known, the analytical expression of which is:

$$K(L_{old}) = \frac{256 \cdot L_{old}}{\pi \cdot d^4} \cdot \frac{\eta_0 \cdot P_{ref}}{T_{ref}^{1+\alpha}} \quad (9)$$

where:

d is the diameter of the column;  
 Pref, Tref are, respectively, the reference pressure and the  
 15 reference temperature (referred to standard conditions);  
 $\eta_0$  is the viscosity of the carrier gas at the reference conditions;  
 $L_{old}$  is the initial length of the column;  
 $\alpha$  is the coefficient depending upon the type of carrier gas used;  
 20 and in which the temperature of said capillary column is maintained equal, instant by instant, starting from the introduction of the mixture into the apparatus, for each analysis of said mixture before and after one of said variations, characterized by the following steps:  

- measuring, prior to said variations, the pressure  $p_{i,old}$  of the carrier gas at the input section of the column, and the pressure  $p_{o,old}$  of the carrier gas at the output section of the column;
- following upon said variations, measuring the new

pneumatic resistance  $KC_{new} = K(L_{new})$  of the column, the analytical expression of which is:

$$K(L_{new}) = \frac{256 \cdot L_{new}}{\pi \cdot d^4} \cdot \frac{\eta_0 \cdot P_{ref}}{T_{ref}^{1+\alpha}} \quad (5)$$

wherein:

5       $L_{new}$  is the new length of the column;

- selecting, after said variations, the new pressure  $p_{o,new}$  at output from the column;
- calculating a new input pressure  $p_{i,new}$  or a new mass flow  $F_{new}$  (referred to standard conditions) of the carrier gas,

10     using the relation:

$$\lambda = \frac{j_{old}}{j_{new}} \cdot g \cdot \frac{p_{o,new}}{p_{o,old}} \quad (1)$$

where:

$$g = \frac{K(L_{new})}{K(L_{old})} = \frac{L_{new}}{L_{old}} \quad (2)$$

$$j_{new} = \frac{3}{2} \cdot \frac{\left( \frac{p_{i,new}}{p_{o,new}} \right)^2 - 1}{\left( \frac{p_{i,new}}{p_{o,new}} \right)^3 - 1} \quad (3)$$

$$j_{old} = \frac{3}{2} \cdot \frac{\left( \frac{p_{i,old}}{p_{o,old}} \right)^2 - 1}{\left( \frac{p_{i,old}}{p_{o,old}} \right)^3 - 1} \quad (4)$$

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- setting, after said variations, said new input pressure  $p_{i,new}$

or said new mass flow  $F_{new}$  of the carrier gas into said apparatus for gaschromatographic analysis in correlation to  $\lambda$ .

2. The method according to Claim 1, in which said method 5 comprises the following steps:

- storing the known quantities  $K(L_{old})$ ,  $K(L_{new})$ ,  $p_{i,old}$ ,  $p_{o,old}$ ,  $p_{o,new}$  in electronic means for storage of said apparatus for gaschromatographic analysis;
- storing the relation  $\lambda$  in said electronic storage means;
- 10 - using  $\lambda$  for calculating and entering said quantity  $F_{new}$  or  $p_{i,new}$ ;
- providing means for setting and control of the input pressure  $p_{i,new}$  and/or of the flow rate  $F_{new}$  in said apparatus for analysis.

15 3. The method according to either Claim 1 or Claim 2, in which for calculation of said input pressure  $p_{i,new}$ , the following relation is used:

$$p_{i,new} = \sqrt{p_{o,new}^2 + \lambda \cdot g \cdot (p_{i,old}^2 - p_{o,old}^2)} \quad (6).$$

4. The method according to Claim 1 or Claim 2, in which for 20 calculation of said mass flow  $F_{new}$ , the following steps are envisaged:

- measuring the mass flow  $F_{old}$ , referred to standard conditions, of the carrier gas before said variations;
- calculating said quantity  $F_{new}$  using the relation:

$$F_{new} = F_{old} \cdot \lambda \quad (7).$$

25 5. The method according to either Claim 1 or Claim 2, in which for the calculation of said mass flow  $F_{new}$ , there are envisaged the steps of:

- measuring, before said variations, the temperature  $T_{col}$  of the capillary column;
- calculating the mass flow  $F_{old}$ , referred to standard conditions, of the carrier gas before said variations, using the relation:

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$$F_{old} = \frac{p_{i,old}^2 - p_{o,old}^2}{KC_{old} \cdot T_{col}^{1+\alpha}} \quad (8)$$

where:

$\alpha$  is the coefficient depending upon the type of carrier gas used;

10  $KC_{old} = K(L_{old})$  is the pneumatic resistance of the column according to relation (5) of Claim 1;

- calculating said quantity  $F_{new}$ , using the relation:

$$F_{new} = F_{old} \cdot \lambda \quad (6).$$

6. The method according to Claim 4 or 5, in which, if the 15 temperature of said capillary column follows a trend which varies in time, the flow  $F_{old}$  is measured or calculated instant by instant, and the flow  $F_{new}$  is calculated instant by instant.

7. The method according to any one of the preceding 20 claims, in which said quantities  $KC_{old} = K(L_{old})$  and  $KC_{new} = K(L_{new})$  are measured by means of blank tests of said gaschromatographic apparatus.

8. An apparatus for gaschromatographic analysis provided with a capillary column that can undergo variation in the length of the column or be replaced with a column having identical real 25 specifications with the exception of the length, and comprising:

- means for measuring the pressure  $p_{i,old}$  of the carrier gas at the input section of the column;

- means for storing the quantities measured, or in any case known,  $p_{i,old}$  (pressure of the carrier gas at input) and  $p_{o,old}$  (pressure of the carrier gas at output), and the quantities:  $K(L_{old})$ , pneumatic resistance of the non-modified column, and  $K(L_{new})$  pneumatic resistance of the column after modification of the length of said column;
- storage and processing means for calculating a new input pressure  $p_{i,new}$  or a new mass flow  $F_{new}$  (referred to standard conditions) of the carrier gas, according to the method claimed in any one of Claims 1 to 7; as well as
- means for setting and control of the input pressure  $p_{i,new}$  and/or of the flow  $F_{new}$ .

9. The apparatus according to Claim 8, characterized in that it comprises means for measuring the mass flow  $F_{old}$  or  $F_{new}$ .

10. The apparatus according to either Claim 8 or Claim 9, characterized in that said means for setting and control of the input pressure  $p_{i,new}$  and/or of the flow  $F_{new}$  are operatively connected to said storage and processing means.

11. The apparatus according to any one of Claims 8, 9 and 10, characterized in that it comprises means for the storage of the quantities  $p_{o,old}$ , the known value of the output pressure for the non-modified column, and  $p_{o,new}$ , the value of the pressure set at output for the modified column.

12. The apparatus according to any one of Claims 8 to 11, characterized in that it likewise comprises means for measuring the output pressure from the column of the carrier gas  $p_{o,old}$  or  $p_{o,new}$ .